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DIPOLE MOMENT OF THE DOUBLE LAYER OF METALLIC SURFACES

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DIPOLE MOMENT OF THE DOUBLE LAYER OF METALLIC SURFACES

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ABSTRACT. The dipole moment is evaluated directly, assuming it to be caused by surface electrons. The occupation of surface levels by s-electrons in the fundamental state is linked to the dipole moment of the double layer.

Oldekop and Sauter [1] have suggested, on the basis of the work of Bardeen /2346[2] [2], the existence of a double layer on the surface of metals in order to explain the difference between the escape potential evaluated using Thomas-Fermi statistics and the measured one. This double layer creates a dipole moment and thus a potential V_{es} in the vicinity of the surface. In contrast to the comparison between predicted and measured values in the alkali cases, Oldekop and Sauter [1] have shown that the potential V_{es} does not represent the essential contribution to the output potential but their method does not permit the accurate evaluation of its exact contribution.

We will attempt to make a direct evaluation of the dipole moment based on the hypothesis that it is caused by surface electrons, whose existence has been shown by Tamm [3]. We do know that in a finite crystal there can exist electronic surface states, whose energy levels have been evaluated in the unidimensional crystalline model where the internal potential is a series of δ-functions [4,5,6].

Moreover, in the case of metals having overlapping bands, Shockley [7] has shown that the introduction of a pair of surface levels involves the suppression of two levels, one in the lower band the one in the upper band as indicated by the pattern in Fig. 1. In the particular case of gold or silver, a surface level will be replaced by a d-electron or an s-electron of the surface atoms.

We now show that the occupation of these surface levels by s-electrons in the fundamental state is necessarily linked to the dipole moment of the double layer proposed by Oldekop and Sauter [1]. Indeed, the center of positive charges is located on the surface itself and since the electron density linked to the surface states depends on the depth x, the center of negative charge will not in general lie on the surface itself and there will result a dipole moment per unit surface $\tau = NeX$, where N is the number of atoms per unit surface and X is the position of the center of negative charge. This moment creates a potential $V_{es} = \tau/2\varepsilon_0$ at a point in the vicinity of the surface.

We evaluate the position X of the center of negative charges from the wave functions

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[1] Submitted by Mr. Louis Neel, Session of February 25, 1963.

[2] Numbers in the margin indicate pagination in the foreign text.

$\Psi_1 = A\,u(x)\,e^{-\mu x}e^{2i\pi(k_y y + k_z z)}$ | inside the crystal ($x > 0$)

$\Psi_2 = B\,e^{\eta x}e^{2i\pi(k_y y + k_z z)}$ | outside the crystal ($x < 0$)

The axis x is perpendicular to the surface, A and B are normalizing constants and $u(x) = \sin[(2\pi/a) + \phi]$, where a is the length of the crystal lattice. The coefficients μ and η can be evaluated from the crystal constants and the energy E corresponding to surface states, and the constants A, B, and ϕ can be found by matching the wave functions on the surface ($x = 0$) at zero angular degrees and normalizing for the whole space. If L_y and L_z denote the crystal dimensions along the y and z axes parallel to the surface, we find

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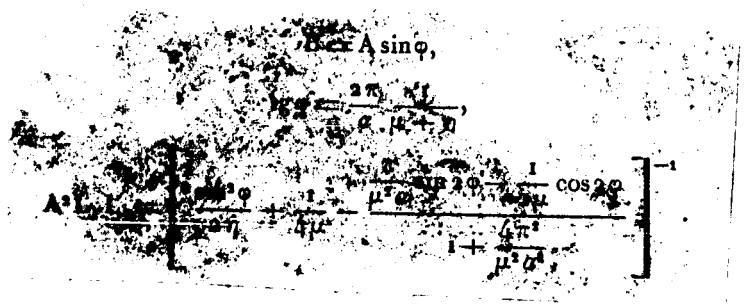

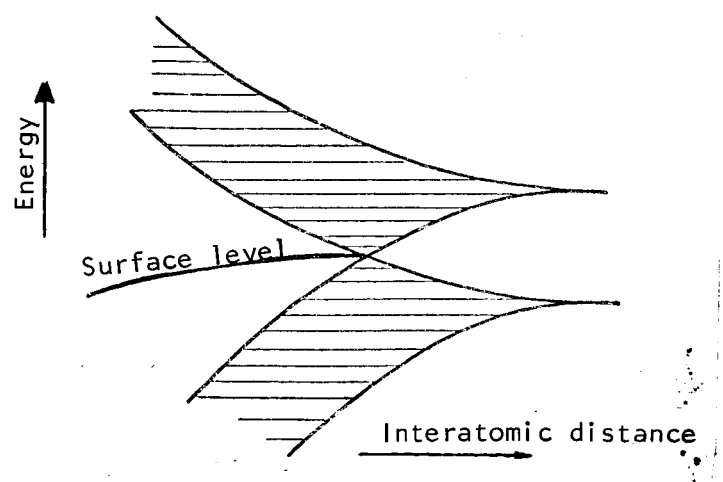

To a wave function ψ, there corresponds an electronic density $\langle\psi|\psi\rangle$ at a point x, y, z. The position of the center of negative charges can be evaluated by writing

$$X = \frac{\langle \Psi | x | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

The integration yields

$$\frac{X}{A^2 L_y L_z} = \frac{1-\cos 2\varphi}{8\mu^2} - \frac{\sin^2\varphi}{4\eta^2} + \frac{\pi}{4}\frac{\sin 2\varphi}{\mu^3 a} + \frac{1}{1+\frac{4\pi^2}{\mu^2 a^2}}\left[\frac{\pi}{2\mu^2 a}\left(\frac{\sin 2\varphi}{2\mu} + \pi\frac{\cos 2\varphi}{\mu^2 a}\right) + \frac{\pi^2}{\mu^3 a^2}\left(\frac{\cos 2\varphi}{2\mu} - \pi\frac{\sin 2\varphi}{\mu^2 a}\right)\right].$$

As an example, we will evaluate the contribution V_{es} to the potential V_0 by taking V_0 = 10 eV and a = 4.04 Å in the case of tight binding. These constants are those of the gold and the self-coherent theory, which converges quickly, giving us a value of $V_{es} \simeq 2V$.

We will show in the near future that the variations of the escape potential with the thickness of the metallic layers [8, 9] are related to corresponding variations in the dipole moment thus evaluated. /2348

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